APPLICATION OF OZONATION IN SANITIZING VEGETABLE PROCESS WASHWATERS

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ABSTRACT

The fresh market carrot industry uses large amounts of water for washing, transporting and cooling for which the present technology for microbial control is chlorination. The concern for chlorination by-products formation and their potential toxicity has created the need for more environmentally friendly water sanitizing approaches. Our research over the past four years has focused on the application of ozonation as a sanitizing method for micrcorganisms in process waters, to assess the control factors effecting concentration requirements of ozone and to develop model systems in predicting the effects of process water constituents (organic and inorganic) on sanitizing functionality of ozone.

Our research group has designed a continuous pilot level test system that includes single or twin mixing tanks fed by a Corona Discharge Ozone Generator supplied by oxygen.

Ozonation of carrot washwaters has resulted in significant reduction in microbial populations.

INTRODUCTION

The fresh market vegetable industry, for example, carrots, uses large amounts of water for washing, transporting and chilling the product. The existing predominant technology for disinfection is chlorination. The concern for the by-products of chlorination and possible toxic chemicals in the water when disposed of has created the need for more environmentally-friendly disinfection techniques. Ozonation meets this need.

Ozone is a highly reactive oxidizing agent with a broad germicidal activity. It has been used as an alternative to chlorine for disinfecting municipal drinking water. Chemically, ozone is *52%* greater in oxidation capacity than chlorine. Present vegetable washing systems utilize chlorine as a disinfectant instead of ozone. These discharges of residual chlorine in waste water may cause the following conditions to occur:

Toxicity of residual chlorine to humans through downstream intake of drinking water
The potential effect of discharges of chlorinated organics formed during the chlorinating of water containing organic substances
The toxic effect of chlorine residuals on aquatic organisms in the receiving waters (Jolley et al., 1984)

Hazards of water chlorination include trihalomethanes (THM) which have been found to have carcinogenic properties of chloroform in rats and mice (Jolley, et al., 1984). Ozone is not expected to leave any residue in the treated water and therefore may be safer than chlorine for disinfecting. Ozone (O_3) has been found to be the most powerful oxidizing disinfectant readily available for water treatment (Rice, et al., 1986). Also, storage of chlorine is dangerous -- another reason for using ozone.

Ozone is presently used in the treatment of industrialized wastewater processes. It is commonly used for the following processes:

Algae removal
Bacterial disinfection
Color removal
Decomplexing organically bound manganese
Increase biodegradability of dissolved organics
Odor control
Oxidation of soluble iron and/or manganese
Preparation of granular activated carbon for biological removal of ammonia and dissolved organics
Destruction of Cyanides
Destruction of organics
Suspended solids breakdown
Viral inactivation (Rice, 1981)

Ozonation is the treatment of a substance with ozone, a highly reactive gas. It is relatively unstable and has a half life of about 20 to 30 minutes in an aqueous solution composed of distilled water at 20 degrees C (68° F). The half life is shorter if reducing materials are present in solution (Rice, 1981).

Ozone acts as an oxidant of the constituent elements of cell walls before entering microorganisms and oxidizing certain essential components (e.g. enzymes, proteins, DNA and RNA). The bacterial or protozoan cells are annihilated after a large part of the cell membrane barrier has been destroyed (Rice and Netzer, 1984).

Ozone Generation

Ozone is most commonly produced by the means of a corona discharge (CD) generator. This is because the corona discharge produces the largest quantities of ozone for the amount of electricity used. In the corona discharge generator, a dry gas containing oxygen (either air or pure oxygen) is passed between two electrically charged plates separated by a ceramic dielectric medium and a narrow discharge gap (Rice, et al., 1986). Under these conditions, as the gas flows through this system, some of the oxygen is transformed according to the following equation:

$$\text{Eq. 1} \quad 3O_2 \rightarrow 2O_3$$

By using the corona discharge ozone generator, concentrations of ozone of 1% -3% are produced with air as the feed gas, and 2% -6% when pure oxygen is the generator feed gas (Rice, et al., 1986). Laboratory studies utilizing ozone for the treatment of tomato washwater have been successful in significantly reducing total aerobic bacterial populations, total coliforms, and fecal coliforms (Williams and Montecalvo, 1993). Similar results are expected in other vegetable crops.

Factors Effecting Mass Transfer Rates

Parameters that normally effect the mass transfer rate include pH, temperature particle size, organic and inorganic concentrations. White (1978) concluded that pH levels between 6 and 8.5 do not seem to significantly effect germicidal efficiency. McGhee (1991) determined the relationship between water temperature and ozone mass transfer efficiency. He found that the higher the temperature of the water, the lower the efficiency of the ozone mass transfer. Consequently, this results in lower germicidal efficiencies at higher water temperatures. Below are some other significant factors which effect the mass transfer of ozone into liquids. They are also effected by the design and operation of the contactor system as follows:

Size of the contactor bubble
Ozone concentration
Humidity
Whether the carrier gas is air or pure oxygen (Rice, 1981)

While ozone is in solution, there are two types of reactions that it may undergo. They have been named direct reactions and indirect reactions (Ram, et al., 1990). Direct reactions are those which occur so rapidly that they are only limited by the rate of mass transfer of ozone into the solution. This is the type of reaction that will occur while treating vegetable washwater. The following compounds will undergo this type of reaction:

Acetic acid
Ammonia
Oxalic acid
Saturated aliphatic alcohols
Urea (Rice, 1981)

Indirect reactions were not addressed in this study.

OBJECTIVES

The overall objective of this project was to assess the effectiveness of ozone to treat vegetable washwater. To accomplish this objective, the following tasks were performed:

1. Design and construct a laboratory-scale test bed apparatus for ozonating water typical of that used for washing fresh market vegetables, in particular, carrots.

2. Perform tests using various mixtures of water, bacteria, organic matter, and inorganic matter that would be representative of the constituents found in a typical vegetable washwater in order to determine the effectiveness ozone as a disinfectant.

3. Determine the parameters for effectively utilizing ozonation to control bacteria in washwater using analyses of the above data.

EXPERIMENTAL SECTION

Design And Construction Of Pilot Test System

The ozonation apparatus is shown in Figure 2. This system utilizes an ozone generator supplied by Clearwater Tech, an ozone equipment manufacturer in San Luis Obispo, CA. The output of this generator, as certified by Clearwater Tech was 2.212% ozone by weight using pure oxygen as a feed gas and at a flow rate of five cubic feet per hour. This was equivalent to 3.77 grams of ozone per hour. This flow rate was used for all testing. The mixing apparatus utilizes a double Venturi gas injector feeding into a Plexiglas cylindrical tank containing approximately 40 liters of water. A second symmetrical tank in tandem allowed for enhanced mixing. In all cases, water and experimental washwaters were circulated using a two horsepower centrifugal pump and appropriate valves.

Experimental Design

This investigation focused on assessing the effectiveness of ozonation as a bacterial disinfectant for water contaminated with various constituents similar to materials and chemical composition found in typical carrot and or similar vegetable washwaters. The selected contaminants included bacteria (Shewanella putrefaciens), organic material (glucose) and inorganic material (bentonite). In addition to these tests, actual carrot washwater was also prepared and ozonated. As shown in Figure 1, tests were performed in which bacteria was introduced into the ozone system, along with organic and inorganic matter. The system was run for thirty minutes during which time samples of the water were taken and analyzed for ozone, temperature, oxidation reduction potential, pH and COD.

Experimental Test Plan

The development of the test plan focused first upon producing a model which established the effect of ozone upon a pure culture of the test organism Shewanella putrefaciens which was chosen based upon its prevalence as a common food spoilage microorganism. Further experiments were conducted in order to establish and document the effects of organic and inorganic loading upon ozone lethality.

Rate Of Ozone Generation

The pilot system was filled with approximately 120 liters of municipal water chilled to 16^{O}C and ozone levels were monitored over a 30 minute period.

Effect Of Ozonation On Bacterial Reduction

Water was first ozonated to a level between 1.5 and 2.0 ppm. At time 0, a pure culture of Shewanella putrefaciens was added to the system and the ozonation system shut off. Samples of water were removed at 0, 1,2.5, 5, 10, 15, 20, 25 and 30 minutes and tested for total aerobic bacterial numbers, pH, temperature, ORP, and ozone concentration.

The next series of experiments involved loading the system with 1000 ppm of glucose then adding the pure culture with continuous ozonation, then loading the system with 1000 ppm of bentonite, adding the pure culture once the ozone levels reached 2 ppm. A third series of experiments involved adding both 1000 ppm of glucose and 1000 ppm of bentonite and the pure culture with continuous ozonation. For each experiment, 50 ml. samples were removed at 0, 1, *2.5,* 5, 10, 15, 20, 25 and 30 minutes and tested for total aerobic bacterial numbers, pH, temperature, ORP and ozone concentration.

Ozonation Of Carrot Washwaters

Ozonation was carried out with actual carrot washwater prepared by washing carrots obtained from a local processor. The whole carrots were washed twice, the first washwater being the dirtiest and the second washwater being similar to the flume water used to transport carrots after they had been washed in the truck. The reason that actual water from the plant was not used was because it already contained chlorine which could mask the effects of ozone. The procedure for ozonation was that approximately 60 liters of clean water was ozonated and circulated through the system for 30 minutes in order to raise the ozone level to 2 ppm or above. Then, approximately 60 liters of each carrot washwater was added and the system parameters were monitored over 30 minutes of continuous ozonation.

Analytical Methodology

Bacterial enumeration was conducted by employing a pour plate technique using trypticase soy agar followed by incubation at 37°C for 48 hours and counting the number of colonies on each plate. For all analysis, the average of triplicate samples were calculated (Standard Methods for the Examination of Water and Wastewater, 1995). pH measurements were conducted using an Orion Ionanalyzer Model 407A after two point calibration. Oxidation reduction potentials were measured with a Cole-Palmer pH-ORP Controller Model 5656-00.

Ozone levels for all analysis were conducted according to the Hach Chemical Co. procedures using either DPD or a Accu Vac Indigo Thiosulfonate Method.

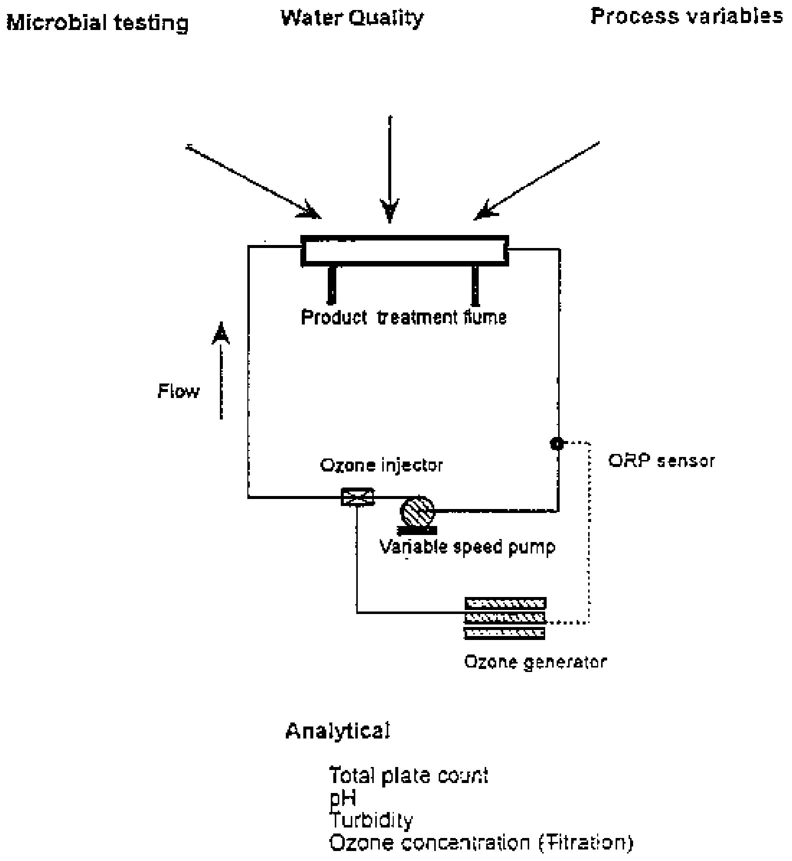


Figure 1 Process Washwater Test System

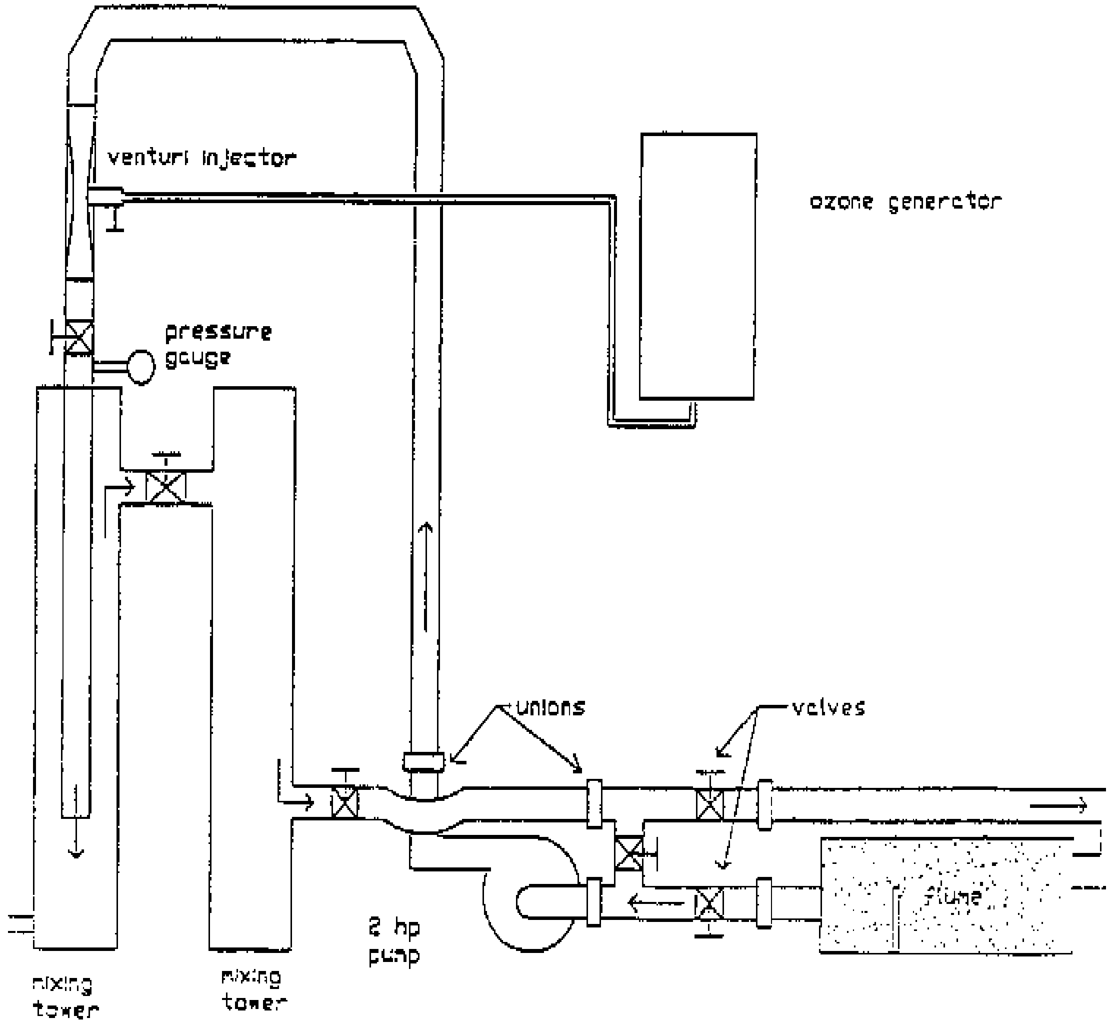


Figure 2 Process Schematic of Ozonation System

Figure 3 - Rate of ozone generation of test system in water at 16° C

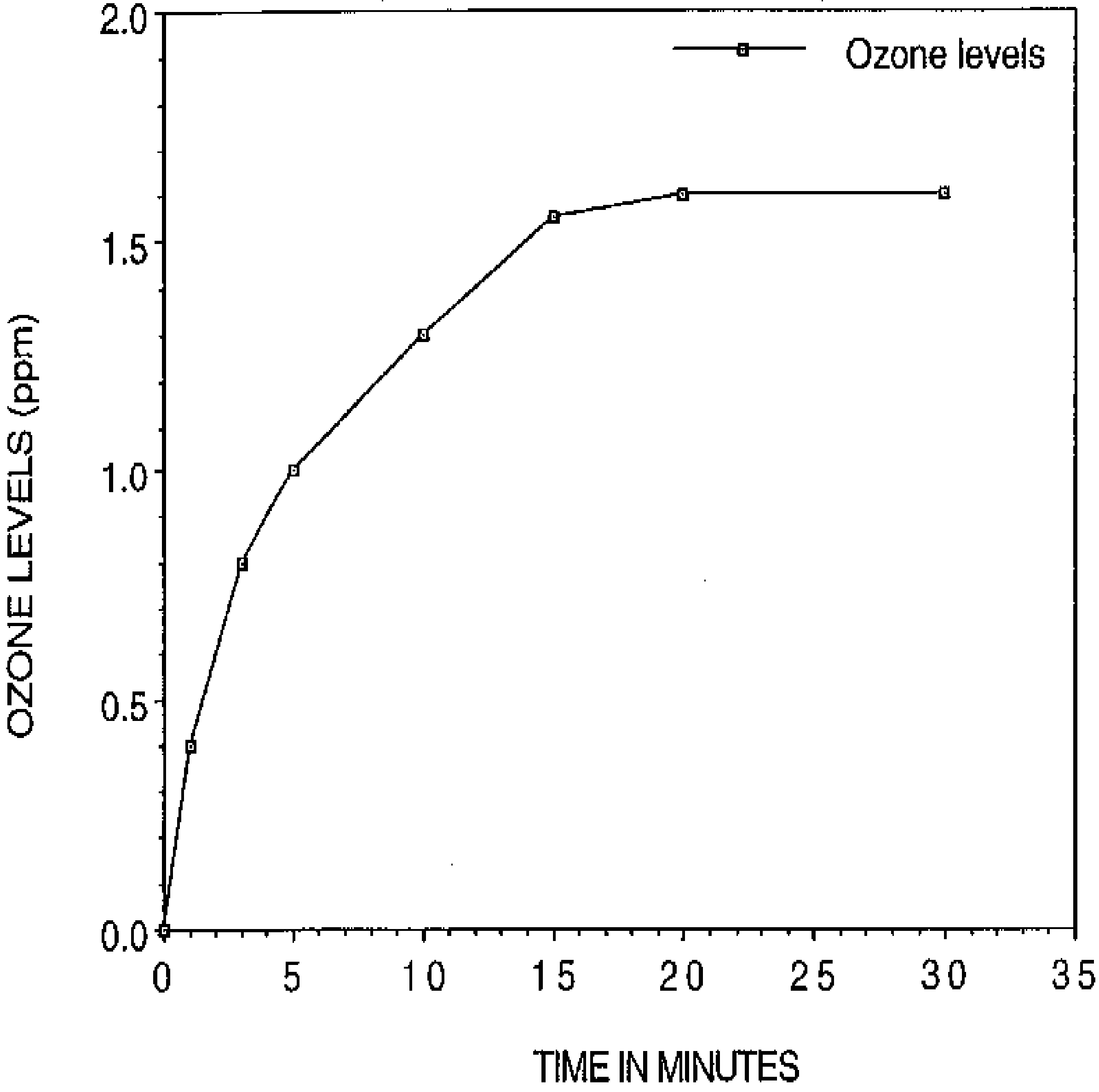


Figure 4 - Effect of ozonation on pure culture levels of ***Shewanella putrefaciens***

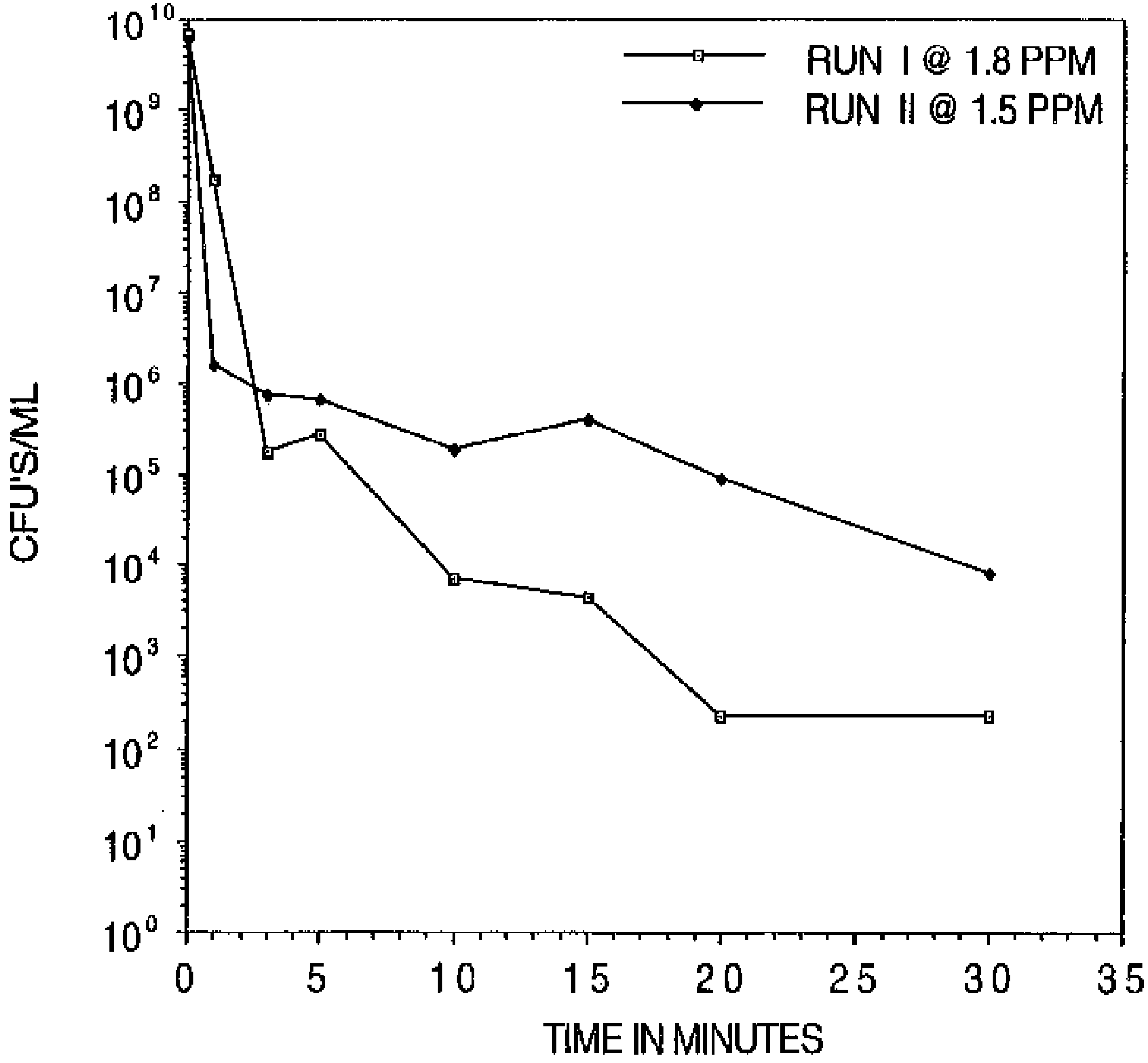


Figure 5 - Effect of 1000 ppm of glucose upon ozone lethality

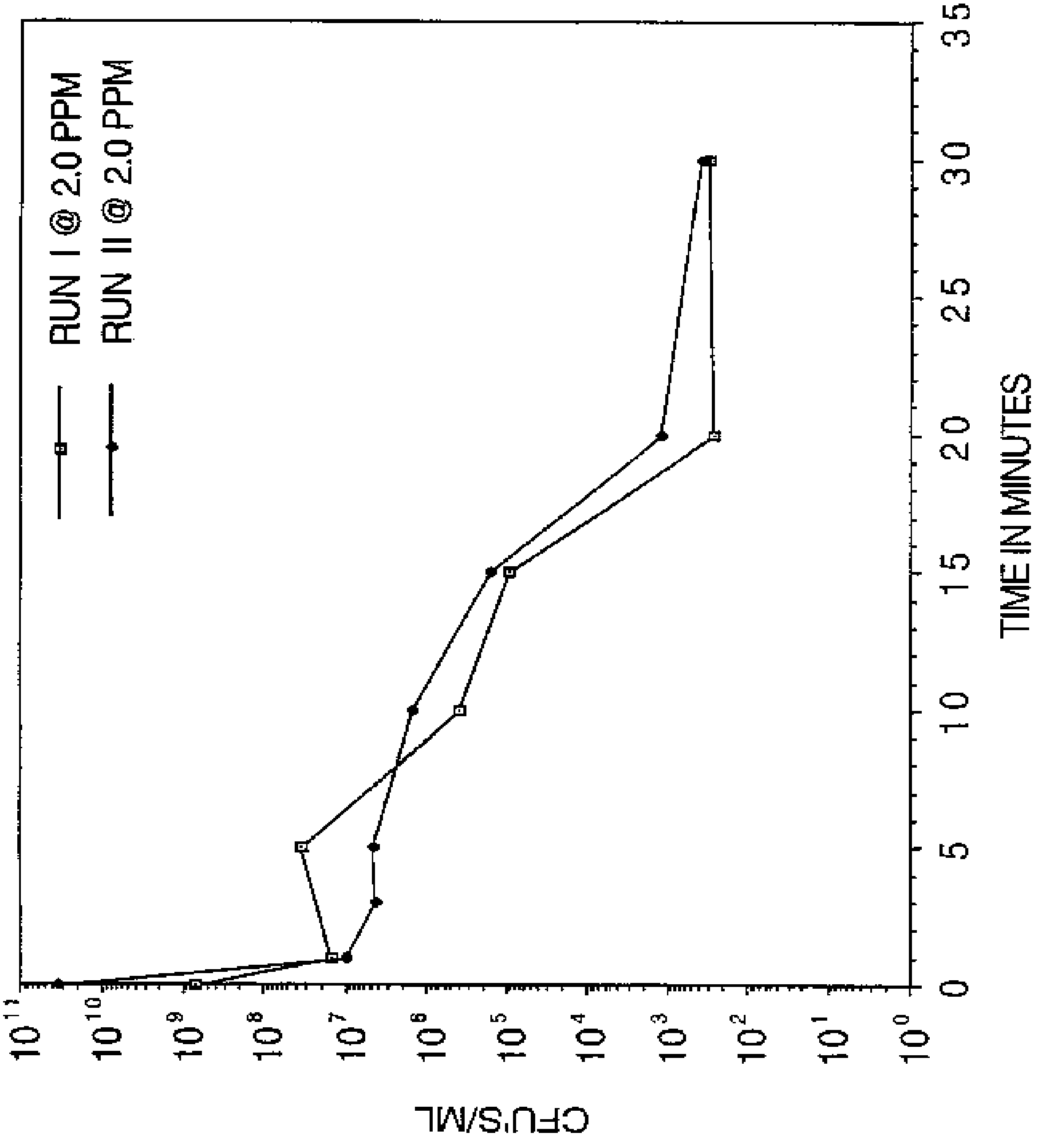


Figure 6 - Effect of 1000 ppm of bentonite on ozone lethality

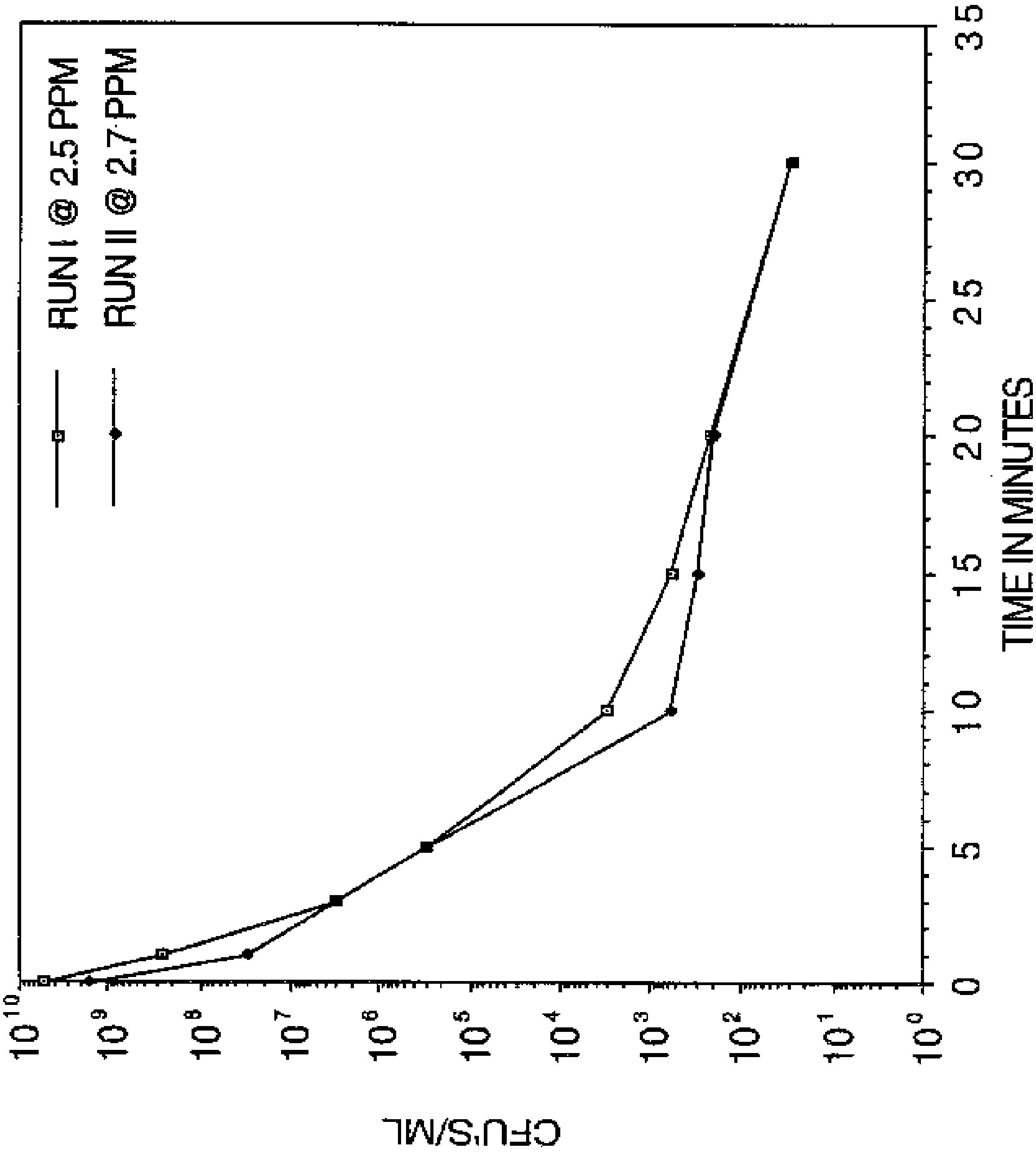


Figure 7 - Effect of both 1000 ppm of bentonite and 1000 ppm glucose on ozone lethality

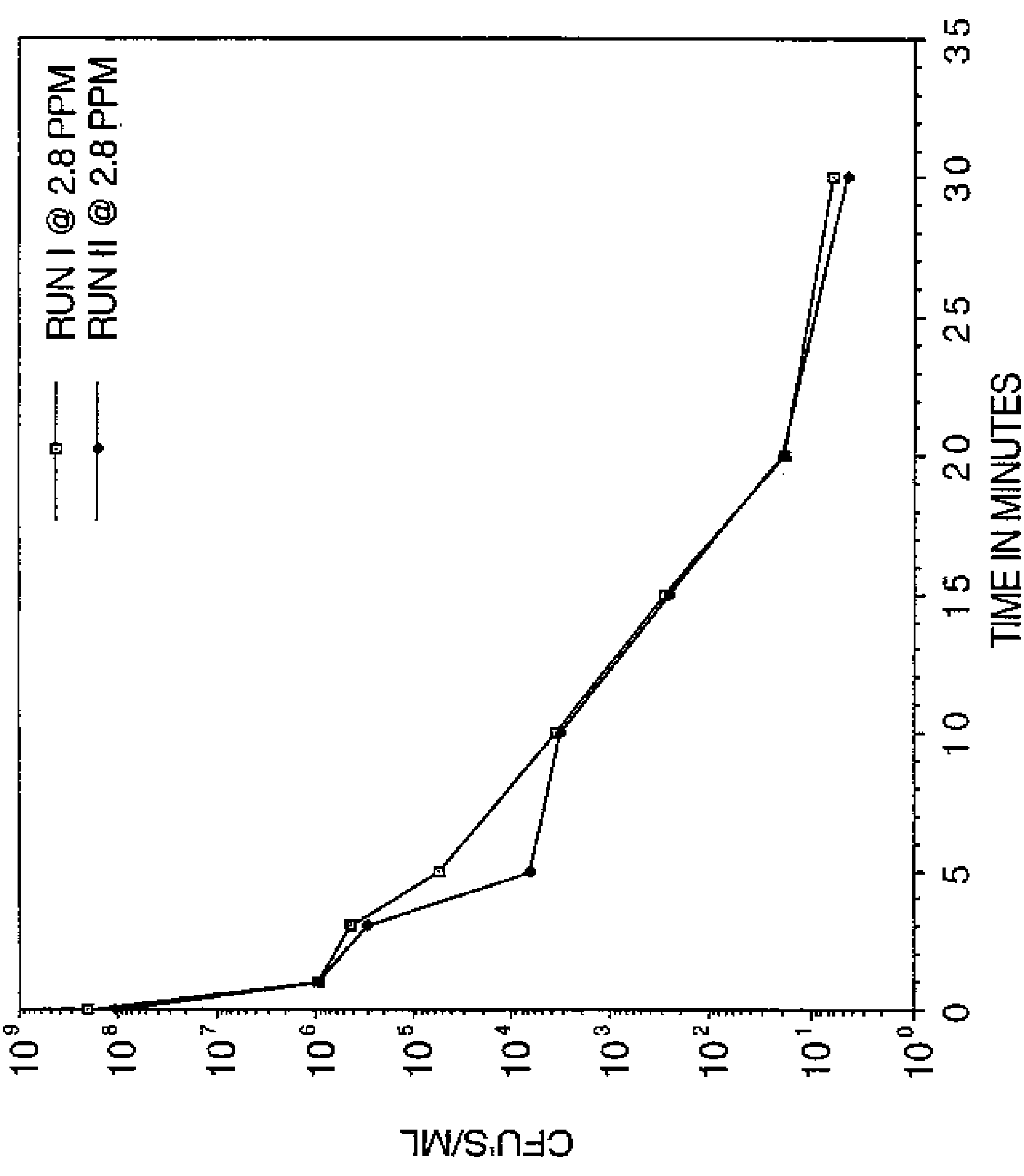
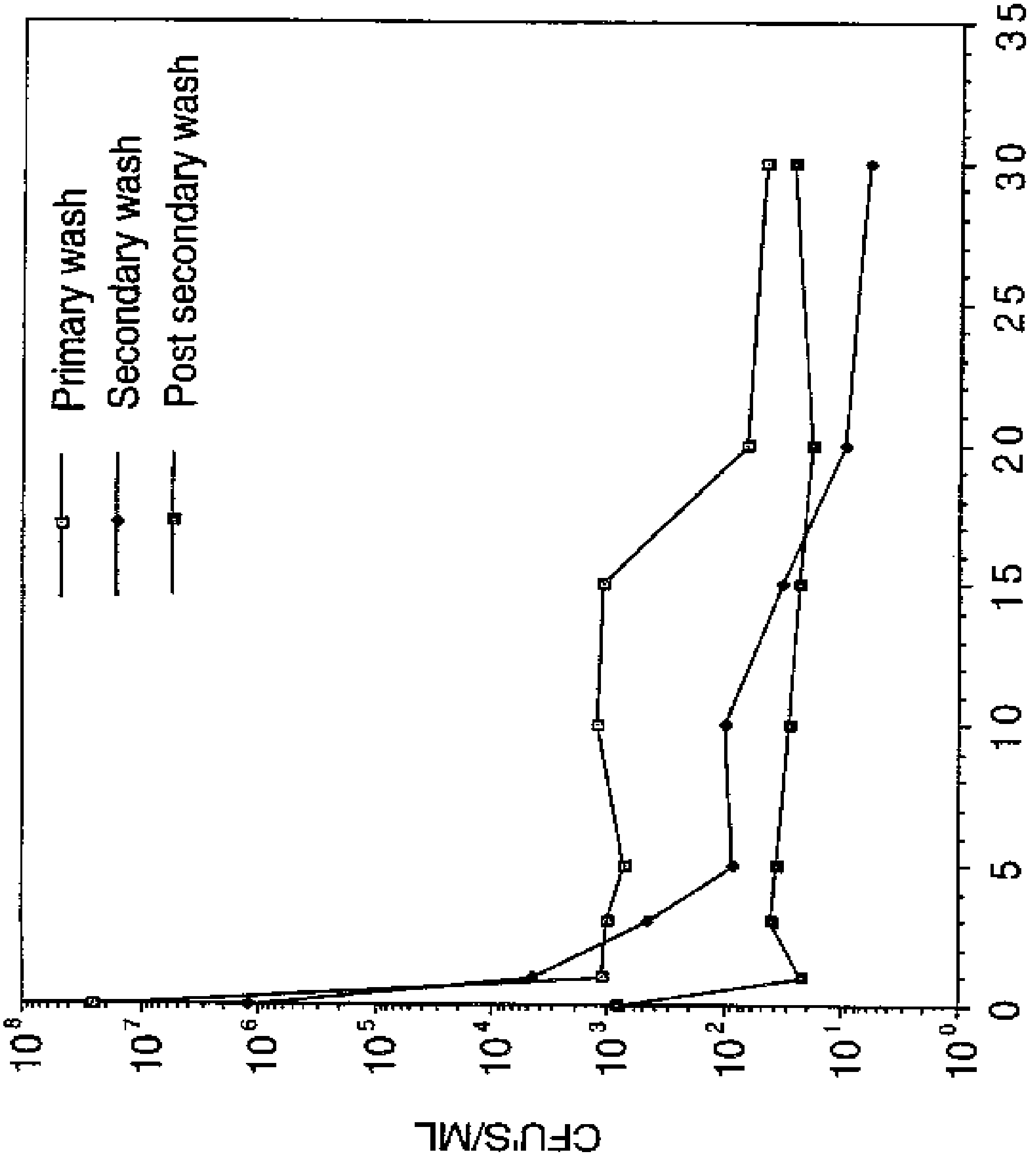


Figure 8 - Effect of ozonation on reduction of total aerobic bacterial populations for carrot wash waters



RESULTS AND DISCUSSION

Figure 3 demonstrates the approximate come-up time of the system. Municipal water was chilled to 15.5 – 16^{O}C, added to the system and ozonated. After 20 minutes of ozonation, ozone levels were consistently between 1.5 and 2.0 ppm. However, since ozone will cause rapid deterioration of gasket materials, we found that by changing the gaskets prior to each experimental run, we were then able to achieve ozone levels exceeding 2.0 ppm. All water temperatures were maintained at 15 – 16^{O}C, since ozone solubility increases as the temperature of the water decreases and this temperature range is the temperature of the washwaters found in vegetable processing plants.

The data shown in Figure 4 was the control in which clean water was used with ozone and with the pure culture of S. putrafaciens. Two liter cultures were centrifuged at 5,000 x G, after having reached the logarithmic phase of cell growth where dead cells are minimal, and added to the system after the water was ozonated in order to bring the concentration up to 1.5 and 2.0 ppm. For both runs, an approximate 4 log cycle reduction in cfu/ml was obtained after five minutes of ozonation. Ozone levels were found to drop initially but recovered to between 0.5 and 1.0 ppm. The ORP readings increased from approximately 400 mu to 1000 mu when the system was ozonated and did not vary when the pure culture was added to the system. Therefore it was concluded that actual ozone measurement will provide a more precise method to monitor the oxidation capacity of the system.

The data shown in Figure 5 profiles the effect of loading the system with 1000 ppm of glucose upon ozone lethality. After 20 minutes of ozonation at an initial ozone concentration of 2.0 ppm a 10^{6} log cycle reduction in cell numbers was observed. During the course of these trials, residual levels of ozone were variable over 1.0 ppm in one run and *0.5* ppm in another. This data does suggest that ozonation is capable of high bacterial lethality even in the presence of high levels of soluble glucose which in turn represented a high level of organic load in the system at 5500 ppm of COD.

The results in Figure 6 further demonstrate the effect of loading the system with 1000 ppm of bentonite upon ozone lethality. For this series of experiments, water was first ozonated to levels in excess of 2.5 ppm, then 1000 ppm hentonite and pure culture were added to the system with continuous ozone generation. After 30 minutes of ozonation a greater than 7 log cycle reduction in bacterial numbers was achieved. This data suggests that bentonite as a source of inorganic loading of the system created little competitive effect on overall process lethality when ozone was used at an initial concentration of greater than 2.5 ppm. After 30 minutes of ozonation residual ozone in the process water did not exceed 0.5 ppm.

Figure 7 shows the combined effects of loading the system with 1000 ppm glucose and 1000 ppm bentionite. Initial ozone concentrations for each run was 2.8 ppm. After 30 minutes of ozonation a 7 log cycle reduction in bacterial numbers was found for both experimental trials. This data further suggests that ozonation under both organic and inorganic combined loading conditions can be very effective when the process water contains between 2.5 and 3.0 ppm soluble ozone.

Figure 8 shows the effects of ozonation on the reduction of total aerobic bacterial populations for carrot washwaters. For this series of experiments, primary carrot washwater (initial washwater) was ozonated at a beginning level of 2.0 ppm. After five minutes of ozonation an approximate 4 log cycle reduction was observed with a further reduction of an additional log cycle after 20 minutes. Secondary washwater representing the rinse water of carrots entering the plant contained an initial level of 10^6 cfu/ml which was reduced to lO^2 cfu/ml. after five minutes of ozonation and to less than 100 cfu/ml after 20 minutes, representing an overall lethality of approximately 5 log cycle reduction. Post secondary washwater, representing transport water in the plant showed an approximate 2 log cycle reduction in cell numbers after ozonation for 30 minutes.

CONCLUSIONS

The results of this study permit the following conclusions:

1. Significant log cycle reductions in bacterial numbers of carrot washwaters can be achieved at ozone levels of 2.0 ppm or greater.

2. Loading of process washwaters with glucose and bentionite, representing organic and inorganic sources of contamination of process washwaters may not significantly effect the ability of ozone to significantly create a high level of sanitizing functionality.

3. Further studies must be conducted to optimize ozone lethality and to further assess the effects of organic and inorganic components of vegetable process washwaters.

4. Further studies should be conducted to evaluate the methods for the quantitative measurement of soluble ozone.

5. Comparative cost evaluations between chlorination and ozonation should be conducted to determine cost competitiveness of ozone at the industry level.

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KEY WORDS

Ozone, vegetable washwaters, carrots, bacteria, pilot level ozonation test system.